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XXV. *Experiments on the Production of artificial Cold.* By Mr. Richard Walker, *Apothecary to the Radcliffe Infirmary at Oxford.* In a Letter to Henry Cavendish, *Esq. F.R.S. and A.S.*

Read June 5, 1788.

THE Royal Society having been pleased to insert, among their Transactions for last year, an account of some experiments of mine, relating to the production of artificial cold, transmitted in a letter from Dr. BEDDOES, I am induced to mention a few I have made since.

Your zealous attention to this subject, under whose auspices this, as well as other branches of natural philosophy, hath received considerable improvement, will, I hope, apologize for the liberty I have taken in addressing myself to you, especially since any new and useful facts I may have ascertained are principally owing to those endeavours your excellent Papers have incited in me.

My most powerful frigorific mixture is the following:

Of strong fuming nitrous acid, diluted with water (rain or distilled water is best) in the proportion of two parts of the former to one of the latter, each by weight, well mixed, and cooled to the temperature of the air, three parts; of vitriolated natron (GLAUBER'S salt) four parts; of nitrated ammonia (nitrous ammoniac) three and a half parts, each by weight, reduced separately to fine powder: the powdered vitriolated

natron is to be added to the diluted acid, the mixture well stirred, and immediately afterward the powdered nitrated ammonia, again stirring the mixture: to produce the greatest effect, the salts should be procured as dry and transparent as possible, and used freshly powdered. These seem to be the best proportions when the temperature of the air and ingredients is $+50^{\circ}$; as the temperature at setting out is higher or lower than this, the quantity of the diluted acid will evidently require to be proportionably diminished or increased. This mixture is but little inferior to one made by dissolving snow in nitrous acid, for it sunk the thermometer from $+32^{\circ}$ to -20° ; perhaps it may be possible to reduce the salts to so fine a powder as to make it equal. In this last experiment the diluted acid was equal in quantity to the vitriolated natron, being four parts each, the nitrated ammonia three and a half as before. A powder composed of muriated ammonia (crude sal ammoniac) five parts, nitrated kali (nitre) four parts, mixed, may be substituted in the stead of nitrated ammonia, with nearly equal effect, and in the same proportion.

Crytallized nitrated ammonia, reduced to very fine powder, sunk the thermometer, during its solution in rain-water, forty-eight degrees, from $+56^{\circ}$, the temperature of the air and materials, to $+8^{\circ}$; and when evaporated gently to dryness, and finely powdered, it sunk the thermometer forty-nine degrees, to $+7^{\circ}$, the temperature of the air and materials being as before at $+56^{\circ}$: therefore, in this salt (which produces, as appears above, much greater cold during solution in water, than any other hitherto known) the water of crytallization is not in the least conducive to that effect. I expected, that by diluting the strong nitrous acid to the proper strength with snow, instead of water, by which its temperature would be much reduced,

reduced, and then adding the salts, a much greater degree of cold might be produced; but, by various diversified trials, I found but little advantage gained; I shall therefore forbear mentioning the particulars. In the course of this winter, some diluted nitrous acid, in a wide-mouthed phial, was immersed in a freezing mixture; when cooled to about -32° , it froze intirely to the consistence of an ointment, when the thermometer suddenly rose to -2° ; on adding some snow that lay by me, it became again liquid, and the mercury sunk into the bulb of a thermometer graduated to -76° : I know not its exact strength; but by the effect imagine it might correspond nearly with that which is capable of the easiest point of spirituous congelation. Cold, I have found, may be produced by the union of such salts as on mixing are decomposed, and become liquid or partially so. The mineral alkali produces this effect with all the ammoniacal salts; but with nitrated ammonia to a considerable degree. The mineral alkali added in powder to nitrous acid, diluted as above, sunk the thermometer twenty-two degrees only, from 53° (temperature of air and materials) to 31° . This salt contains nearly as much water of crystallization as vitriolated natron, and produces more cold during solution in water than that salt. The reason why it produces less when added to acid than the neutral salt does, is perhaps sufficiently evident. I have observed the thermometer to be stationary, or even to rise, during the violent effervescence produced on mixing those materials, and to sink as soon as that ceased.

Vitriolated natron dissolved indifferently in rectified spirit of wine, and produced neither heat or cold; the disposition to produce cold, during its solution, being perhaps exactly counteracted by the tendency which the dissolved salt hath in

uniting with the spirit to produce heat. Vitriolated magnesia (a salt very similar to vitriolated natron) during solution in the diluted nitrous acid, produced nearly as much cold as that salt: the small difference there is between them, as to this effect, may be owing to the former containing rather less water in its crystals.

Vitriolated natron, liquified by heat, was set to cool; when its temperature was reduced to 70° , it became solid, and the thermometer immediately rose to 88° (eighteen degrees) its freezing point. Does not the quantity of sensible heat evolved by this salt, in becoming solid, indicate its great capacity for heat, in returning to a liquid state, and consequently account in a great measure for its producing such intense cold during solution in the diluted mineral acids? Two salts, vitriolated argillaceous earth (alum) and tartarized natron (Rochelle salt), each contain nearly as much water of crystallization as vitriolated natron; but produced neither of them any considerable effect during solution in the diluted nitrous acid; the latter made the thermometer rise: neither did their temperatures increase, like that salt, in changing from a liquid to a solid state.

From the obvious application of artificial frigorific mixtures to useful purposes, in hot climates especially, where the inhabitants scarcely know by the sense of feeling winter from summer, it may not be amiss to hint at the easiest and most economical method of using them. For most intentions, perhaps, the following cheap one may be sufficient: of strong vitriolic acid, diluted with an equal weight of water, and cooled to the temperature of the air, any quantity; add to this an equal weight of vitriolated natron in powder: this is the proportion when the temperature set out with is $+50^{\circ}$,

and will sink the thermometer to 5° ; if higher, the quantity of the salt must be proportionably increased. The obvious and best method of finding the necessary quantity of any salt to produce the greatest effect, by solution in any liquid, at any given temperature, is by adding it gradually until the thermometer ceases to sink, stirring the mixture all the while.

If a more intense cold be required, double aqua fortis, as it is called, may be used; vitriolated natron, in powder, added to this, produces very nearly as much cold as when added to the diluted nitrous acid: it requires a rather larger quantity of the salt, at the temperature of $+50^{\circ}$, about three parts of the salt to two parts of the acid: it will sink the thermometer from that temperature nearly to 0, and the consequence of more salt being required is, its retaining the cold rather longer. This mixture has one great recommendation, a saving of time and trouble. A little water in a phial, immersed in a small tea-cup of this mixture, will be soon frozen in summer; and if the salt be added in crystals unpounded to double aqua fortis, even at a warm temperature, the cold produced will be sufficient to freeze water or creams; but if diluted with one-fifth its weight of water, and cooled, it is about equal to the diluted nitrous acid above mentioned, and requires the same proportion of the salt. A mixture of vitriolated natron and diluted nitrous acid sink the thermometer from $+70^{\circ}$ (temperature of air and ingredients) to $+10^{\circ}$.

The cold in any of these mixtures may be kept up a long time by occasional additions of the ingredients in the proportions mentioned. A chemist would make the same materials serve his purpose repeatedly.

Equal parts of muriated ammonia and nitrated kali in powder make a cheap and convenient composition for producing cold

cold by solution in water; it will, by the following management, freeze water or creams at Midsummer.

June 12th, 1787, a very hot day, I poured four ounces, wine measure, of pump-water, at the temperature of 50° (it is well known that water at springs retains nearly the same temperature winter and summer, *viz.* about 50° , to which temperature the water may be reduced during the warmest weather, by pumping off some first) upon three ounces, Avoirdupois weight, of the above powder (previously cooled by immersing the vessel containing it in other water at 50°), and after stirring the mixture its temperature was 14° ; some water contained in a small phial, immersed in this mixture, was consequently soon frozen. This solution was afterwards evaporated to dryness, in an earthen vessel, reduced to powder, and added to the same quantity of water, under the same circumstances as before, when it again sunk the thermometer to 14° . Since that time I have repeatedly used a composition of this kind for the purpose of producing cold, without observing any diminution in its effect after many evaporations. The cold may be economically kept up and regulated any length of time, by occasionally pouring off the clear saturated liquor, and adding fresh water, observing to supply it constantly with as much of the powder as it will dissolve.

The degree of cold at which water begins to freeze has been observed to vary much; but that it might be cooled twenty-two degrees below its freezing point was perfectly unknown to me until lately. I filled the bulb of two thermometers, one with the purest rain-water I could procure, the other with pump-water; the water was then made to boil in each, until one-third only remained: these were kept in a frigorific mixture, at the temperature of $+10^{\circ}$, for a much longer time than

than I thought necessary to cool the water to the same temperature; and by repeated trials I found it was necessary to lower the temperature of the mixture to near $+5^{\circ}$, to make the water in either of them freeze. These were likewise suspended out of doors, close to a thermometer, during the late frost, and the water never observed frozen. On March the 22d, at six in the morning, the water in each remained unfrozen, though the tubes were gently shaken, the thermometer standing at that time at 23° . There appeared to be little difference with respect to the degree of cold necessary to freeze the water, whether the tube of the thermometers were open or closed in vacuo (which was very nearly effected by suffering the water to boil up to the orifice of the tube, and then suddenly sealing it) or not, but unboiled water in the same situation froze in a higher temperature.

It is commonly supposed, I believe, that gentle agitation of any kind will dispose water (cooled below its freezing point) to become ice; but I have repeatedly cooled rain-water and pump-water, boiled a long time, and unboiled, in open vessels to 30° or lower, and have constantly succeeded, after trying other kinds of agitation in vain, by stirring, or rather scraping gently, the bottom and sides of the vessel containing the water to be frozen, when after some short time small filaments of ice appeared, and by continuing this motion about every part of the vessel beneath the surface of the water, about two-thirds of the water commonly froze. A slender, pointed glass rod I used for this purpose.

I have the honour to be, &c.

RICH. WALKER.

Oxford, March 27, 1788.

Extract from a second Letter from Mr. Walker to Henry Cavendish, Esq. Dated Oxford, May 28, 1788.

A more intense cold may be produced by a solution of salts in water in summer, than can be produced by a mixture of snow and salt in winter. To rain-water six drachms (by weight) I added six drachms of nitrated ammonia reduced to a very fine powder which made the thermometer sink from $+50^{\circ}$ (temperature of the materials) to 4° , then adding six drachms of mineral alkali very finely powdered the thermometer sunk to -7° , fifty-seven degrees. It is observable, that in the latter there are two causes concur in producing the effect, the liquifaction both of the snow and salt; but in the experiment just mentioned the liquifaction of the salts only.

Vitriolated natron, after it had given out its water of crystallization by exposure to the atmosphere, produced no change of temperature by solution in the diluted nitrous acid, but during solution in water produced heat, as did likewise the mineral alkali.

I have since my last seen FAHRENHEIT's Experiments on the freezing of Water, related in Vol. XXXIII. of the Philosophical Transactions; but as mine differ in degree I take no farther notice of them.

